COMPARISON BETWEEN HALOGENATED AND PHOSPHORUS-CONTAINING FLAME RETARDANTS IN POLYBUTHYLENETEREPHTALATE: TOXICOLOGICAL AND ECOTOXICOLOGICAL EVALUATION OF THE COMBUSTION PRODUCTS

N. Milanov[1], K. Doods[1], K.-W. Schramm[1], G. Matuschek[1], D. Lenoir[1], A. Kettrup[1,2]

[1]GSF - Research Center for Environment and Health, Institute for Ecological Chemistry, Ingolstaedter Landstrasse 1, D-85764 Neuherberg, Germany

[2]Technische Universität München, Lehrstuhl für Ökologische Chemie und Umweltanalytik, Weihenstephaner Steig 23, D-85350 Freising, Germany

Introduction

Incorporated into polymers, flame retardants undergo combustion in industrial waste incinerators. In addition, in case of accidental fires, burning processes are of different type and the composition of the evolved emissions varies from these under controlled thermal disposal. As far as they are considered as directly hazardous to health and the environment, the question of their toxicological and ecotoxicological impact is of great interest and is closely related to the product-integrated environmental protection.

One of the most common groups of flame retardants for a large number of polymers nowadays is the group of halogenated compounds because of their good technical properties and relatively low price. However, numerous investigations have proved formation of incineration products with high toxicity. For example large formation rates of polybrominated dibenzodioxins and -furanes (PBDD/F) were observed from the combustion of ether-type brominated flame retardants, such as penta-, octa- and decabromodiphenyl ether [(1,2)]. Moreover, some brominated flame retardants possess high persistence [(3)] and easily accumulate in humans and animals. That is why there are many attempts for restriction of the bromine content and development of substitute products. A good alternative is the use of phosphorus containing flame retardants, which can be applied to a growing number of different polymers. Many phosphorus flame retardants meet the high requirements for fire protection and additive polymer compatibility.

In our studies oxidative thermal degradation of polybuthyleneterephtalate (PBT) was performed under standardized laboratory conditions. The non-fire-retarded polymer was compared to bromine and phosphorus based flame-retarded PBT. The captured incineration products were subjected to a cell toxicity test and an aquatic ecotoxicological test.

Materials and methods

Differently retarded and non-retarded fiberglass reinforced PBT was used in the study. The compounds used as fire retardants were an alkyl-phosphinic acid salt (10 %) and brominated polystyrene (14 %) with Sb_2O_3 (3,5 %) as synergist. Beech wood was used as reference material, since beech wood smoke is widely used in the food industry to cure meet or fish.

The model incinerations were performed in a BIS-oven (German Standard Method DIN 53436 [(4)]) in air atmosphere at three different temperatures: 400 °C, 600 °C and 800 °C. Triple incinerations of all

the materials (250 mg of sample for each incineration) were carried out for the bioluminescence test. For the EROD test the sample amounts of 1 g were burned. The residence time of the samples in the furnace was 10 minutes and synthetic air was continuously supplied into the system with a flow rate of 150 ml/min. The semi- and low-volatile combustion products were captured in a liquid nitrogen cooling trap and dissolved in 3,5 ml water (for the aquatic bioluminescence test) or in 3,5 ml toluene (for the cell EROD test).

Bioluminescence test

An ecotoxicological acute toxicity assay with the luminescent bacteria LCK 482 (*Vibrio fischeri* NRRL-B-11177) was performed according to the international standard ISO DIS 11348 (German Standard Method DIN 38412 [5]). Double determinations of each crude water extract, in 9 dilution levels for each measurement, were performed on LUMIStox 300 photometer (Dr. Bruno Lange GmbH & Co. KG). All water used (including the water for trapping the combustion products) was purified using a Milli-Q Ultrapure Water System with resistivity 18.2 Megaohm-cm (Millipore Corp.).

EROD test

The EROD activity was determined according to Donato et al. with some modifications [6]. The following clean-up procedure was applied to the crude toluene extracts: At first the glass columns were dried-filled from bottom to top with 10 g active silica (mesh 63-200 µm), 20 g acid silica (44 % concentrated sulfuric acid w/w) and 40 g inactive silica (4 % water w/w). Each column was topped with Na_2SO_4. After conditioning the concentrated crude extracts of samples (1 g) were eluted with 870 ml n-hexane and 8,7 ml methylene chloride. The eluates were reduced by evaporation (550 mbar, 333 K) to 2-3 ml. The extracts were transferred stepwise into vials and evaporated to dryness under a steam of nitrogen. Samples were redissolved in 500 µl of DMSO:isopropanol (4:1 v/v) [7].

Results and discussion

Bioluminescence test

In order to be able to compare toxicities of the combustion products from the selected materials all the data are related to the weight of the samples before the incineration [8]. The EC_{50} values were determined for an incubation period of 30 minutes.

The results of toxicity tests with the luminescent bacteria show an increasing toxicity of the combustion products from all of the investigated materials with increasing incineration temperature. The toxicity of the emissions formed at 400 °C is much lower than the one at 600 °C and 800 °C. Only beech wood behaves differently showing lowest toxicity at 600 °C. The other exception is the emission from PBT protected with brominated polystyrene, which shows highest toxicity at 600 °C.

Sorted by incineration temperatures, the toxicities of the different emissions show the following trend: The most toxic products to the luminescent bacteria at 400 °C are released by beech wood, followed by the emissions from the PBT protected with the phosphinic acid salt. The toxicity of the combustion products from the PBT retarded with brominated polystyrene is several times lower than for these two. At 600 °C and 800 °C the most toxic are emissions from the non-retarded PBT. The addition of phosphinic acid salt to PBT does not change the toxicity of the combustion products. The incineration products from beech wood are about three times less toxic than for these two. Again, as at 400 °C, the PBT protected with brominated polystyrene appears to produce the less toxic emissions from the chosen materials.

It should be kept in mind that these results are based on the total sample weight, not to the amount of PBT or flame retardant in each sample.

EROD test

The EROD test was performed for the incineration products from the PBT protected with brominated polystyrene and phosphinic acid salt formed at 600 °C. The international toxic equivalents (I-TEQs) were determined for incubation periods of 24 and 72 hours. While the results for the emission from phosphinic acid salt-retarded PBT show no effects after 72 hours, the combustion products from brominated polystyrene-retarded PBT appear to be persistent and exhibit higher I-TEQ values.

Acknowledgements

We would like to thank Miss Popp for the valuable help in performing the bioluminescence test.

References

1. Lenoir D. and Kampke-Thiel K. (1995) in: Fire and Polymers II: Materials and Tests for Hazard Prevention (Nelson G., Ed.), American Chemical Society, ISBN 0841232318
2. Dumler R., Lenoir D., Thoma H. and Hutzinger O. (1989) Journal of Analytical and Applied Pyrolysis, 16, Issue 2, 153-158
3. C. A. de Wit (2002) Chemospere, 46, 583-624
4. DIN 53436-1 (1981) Erzeugung thermischer Zersetzungsprodukte von Werkstoffen unter Luftzufuhr und ihre toxikologische Prüfung; Zersetzungsgerät und Bestimmung der Versuchstemperatur
5. DIN 38412 part 34 (1989) Bestimmung der Hemmwirkung von photobacterium phosphoreum (Leuchtbakterien-Abwassertest mit lyophilisierten Bakterien)
6. Donato M. T., Gómez-Lechón M. J., Castell J. V. (1993) Analytical Biochemistry, 213, Issue 1, 29-33
7. Schwirzer S. M., Hofmaier A. M., Kettrup A. A., Nerdinger P. E., Schramm K. W., Thoma H., Wegenke, M., Wiebel F. J. (1998) Ecotoxicology and Environmental Safety, 41, Issue 1, 77-82
8. Kettrup A. A., Lenoir D., Thumm W., Kampke-Thiel K. and Beck B. (1996) Polymer Degradation and Stability, 54, 175-180